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(71) Applicant: **Nippon Steel & Sumitomo Metal Corporation**
Tokyo 100-8071 (JP)

(72) Inventors:
- **HASEGAWA, Hajime**
  Tokyo 100-8071 (JP)
- **YAMADA, Wataru**
  Tokyo 100-8071 (JP)
- **KIYOSE, Akihito**
  Tokyo 100-8071 (JP)
- **KUDOU, Kouichi**
  Tokyo 100-8071 (JP)
- **YAMASAKI, Shingo**
  Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4
81675 München (DE)

(54) HIGH-CARBON STEEL WIRE HAVING EXCELLENT DRAWABILITY AND FATIGUE PROPERTIES AFTER DRAWING

(57) High performance high carbon wire with refined inclusions after wire rolling, extremely low wire breakage rates at the time of drawing even in tough applications, and excellent in fatigue characteristics after wire drawing, characterized by having a predetermined composition of ingredients and in that the number ratio of inclusions satisfying $(\%SiO_2)$=40 to 95%, (%can)=0.5 to 30%, $(\%Al_2O_3)$=0.5 to 30%, (%MgO)=0.5 to 20%, and (%MnO) =0.5 to 10% and further satisfying (%Na)=0.2 to 7% and (%F)=0.17 to 8% (below, referred to as "inclusions covered due to composition") in the oxide-based nonmetallic inclusions of a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter (area converted to diameter) of 1 μm or more which are seen in the L direction cross-section of the wire (below, referred to as "inclusions covered due to size"), that is, the number of inclusions covered due to composition/number of inclusions covered due to size×100, is 80% or more.

EP 2 682 489 A1

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Description

Technical Field

[0001] The present invention relates to wire for drawing purposes, in particular high carbon steel wire and wire for valve springs which are excellent in drawability and fatigue characteristics after drawing.

[0002] The wire of the present invention is used, after drawing, for example, for steel cord for automobile tires, saw wire for cutting silicon for solar cells or semiconductors, valve springs for automobile engines, long rubber belts, aircraft tires, bridge ropes, etc.

Background Art

[0003] In general, high carbon steel wire which is used for drawing purposes has to be able to be drawn at a high speed and has to be excellent in fatigue resistance after drawing. As one of the factors having a detrimental effect on these characteristics, hard oxide-based nonmetallic inclusions may be mentioned.

[0004] Among these oxide-based inclusions, inclusions of Al_2O_3, SiO_2, CaO, TiO_2, MgO, and other single-composition or binary systems of $MgO \cdot Al_2O_3$ or $2MgO \cdot SiO_2$ are high in hardness and nonviscous. Therefore, to produce high carbon steel wire excellent in drawability, it is necessary to raise the cleanliness of the molten steel and soften the oxide-based inclusions.

[0005] As the method of raising the cleanliness of steel and softening nonmetallic inclusions in this way, PLT 1 shows a method of production of steel for high carbon steel excellent in drawability. PLT 2 discloses a method of production of extremely fine wire. The basic idea of these arts is limited to three-component system oxide-based nonmetallic inclusions of Al_2O_3-SiO_2-MnO.

[0006] PLT 3 proposes making nonmetallic inclusions the Spessartite region in a Al_2O_3, SiO_2, MnO three-component phase diagram so as to improve the drawability of the product. PLT 4 discloses a method of restricting the amount of Al which is added to the molten steel so as to reduce harmful inclusions and improve the drawability.

[0007] PLT 5 relates to production of steel cords of a nonviscous inclusion index of 20 or less and proposes to blow CaO-containing flux together with a carrier gas (inert gas) into the ladle molten steel while completely restricting Al so as to perform preliminary deoxidation, then blow in an alloy which contains one or more of Ca, Mg, and REM and thereby soften the inclusions.

[0008] Among the above methods, with the method of reforming ternary nonmetallic inclusions, stable control of the composition is difficult. On the other hand, with the method of control of multi-component nonmetallic inclusions, it is difficult to reduce the size and number of inclusions and secure the ductility. Therefore, it is difficult to improve the drawability and fatigue resistance after drawing.

[0009] Therefore, PLT 6 restricts the range of the total oxygen content to a certain range to control the amount and composition of the nonviscous inclusions, reduces the size and number of nonviscous inclusions and secures ductility to thereby make the amount and distribution of size of nonviscous inclusions the preferable state, further, adds the composition of inclusions to SiO_2 and MnO, and reforms them to multi-component oxide-based inclusions which selectively contain Al_2O_3, MgO, CaO, and TiO_2 so as to soften the inclusions and realize high carbon steel wire extremely excellent in drawability and fatigue resistance after drawing.

[0010] Furthermore, PLT 7 discloses the method of limiting the sizes of hard high SiO_2 inclusions and reducing the amount of use of expensive deoxidizing alloys.

[0011] Further, for control for facilitating stretching of nonmetallic inclusions at a lower melting point, several methods of utilizing alkali metal compounds have been proposed. PLT 8 proposes to use a mixture of an Si-based deoxidizing agent and an alkali metal compound so as to control the amount of alkali metal compound in the nonmetallic inclusions to 4 to 24% and improve the stretchability.

[0012] Furthermore, PLT 9 proposes Si-killed steel which is excellent in fatigue strength characterized by including 0.5 to 10% of an oxide of an alkali metal in Al_2O_3-CaO-SiO_2-MgO-MnO-based low melting point inclusions.

[0013] Furthermore, PLTs 10 and 11 disclose steel wire for high cleanliness springs excellent in fatigue characteristics characterized by including one or more of LiO_2, Na_2O, and K_2O in a total of LiO_2, Na_2O, and K_2O of 0.5 to 20% in low melting point inclusions. These describe that LiO_2, Na_2O, and K_2O are not equal and that by positively adding Li with its particularly strong deoxidizing power as the source of formation of the oxide-based inclusions, the effect is raised if including a suitable amount of LiO_2 in the oxide-based inclusions.

Citations List

Patent Literature

[0014]

PLT 1: Japanese Patent Publication No. 57-22969B
PLT 2: Japanese Patent Publication No. 55-24961A
PLT 3: Japanese Patent Publication No. 54-7252B
PLT 4: Japanese Patent Publication No. 50-81907A
PLT 5: Japanese Patent Publication No. 57-35243B
PLT 6: Japanese Patent Publication No. 4-8499B
PLT 7: Japanese Patent No. 3294245A
PLT 8: Japanese Patent No. 2654099A
PLT 9: Japanese Patent No. 3719131A
PLT 10: Japanese Patent Publication No. 2005-29888A
PLT 11: Japanese Patent No. 4315825B

Non-Patent Literature

[0015] NPLT 1: Iron and Steel Institute of Japan ed. Third Edition Iron and Steel Handbook, II. Iron-making and Steel-making, page 690

Summary of Invention

Technical Problem

[0016] As explained above, by securing the cleanliness of the molten steel, softening the nonmetallic inclusions, preventing contamination by Al, etc., high carbon steel wire which has a high drawability could be supplied.

[0017] In this regard, in recent years, an improvement in productivity has been sought by elimination of the patenting after primary drawing in the process of drawing wire. Also, the market for saw wire finer than the steel cord used for automobile tires has grown. Therefore, the size of inclusions in wire causing breakage has become much smaller than the past (20 μm or more). With only conventional inclusion softening art, the inclusions cannot be sufficiently stretched and handling becomes difficult.

[0018] The present invention was made in consideration of the above situation and has as its topic the supply of high performance high carbon wire which is able to handle even tough applications, which is extremely low in wire breakage rate at the time of drawing, and which is excellent in fatigue characteristics after wire drawing by utilizing the basic technique of multi-component control of oxide-based nonmetallic inclusions and utilizing compounds other than oxides so as to cause a distinctive drop in the melting point and viscosity of nonmetallic inclusions and refine the inclusions after wire rolling.

Solution to Problem

[0019] The inventors investigated in detail the relationship between the composition of nonmetallic inclusions and the melting point or viscosity. As a result, they discovered that by establishing the copresence of Na or another alkali metal and a fine amount of fluorine in multi-component inclusions, it is possible to further lower the melting point and viscosity of inclusions, possible to control the formation of the crystal phases, and as a result possible to refine the inclusions after wire rolling.

[0020] Furthermore, the inventors discovered that there is also the effect of delaying the formation of crystal phases of nonmetallic inclusions in the NaF molecules.

[0021] The present invention was made based on the above discovery and has as its gist the following.

[0022] (1) High carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing which contains, by mass%, C: 0.5 to 1.2%, Si: 0.15 to 2.5%, Mn: 0.20 to 0.9%, $P \leq 0.025\%$, S: 0.004 to 0.025%, Al: 0.000005 to 0.002%, Ca: 0.00001 to 0.002%, Mg: 0.00001 to 0.001%, Na: 0.000005 to 0.001%, and F: 0.000003 to 0.001%, has a total oxygen amount of 16 to 30 ppm, and has a balance of Fe and unavoidable impurities, the high carbon steel wire rod characterized in that the number ratio of inclusions satisfying ($\%SiO_2$)=40 to 95%, (%CaO)=0.5 to 30%, ($\%Al_2O_3$) =0.5 to 30%, (%MgO)=0.5 to 20%, and (%MnO)=0.5 to 10% and further satisfying (%Na)=0.2 to 7% and (%F)=0.17 to 8% (below, referred to as "inclusions covered due to composition") in the oxide-based nonmetallic inclusions of a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter (area converted to diameter) of 1 μm or more which are seen in the L direction cross-section of the wire (below, referred to as "inclusions covered due to size"), that is, the number of inclusions covered due to composition/number of inclusions covered due to sizex 100, is 80% or more:

[0023] where (%SiO_2), (%CaO), (%Al_2O_3), (%MgO), (%MnO), (%Na), and (%F) respectively are the contents of SiO_2, CaO, Al_2O_3, MgO, MnO, Na, and F in the inclusions (mass%). (Same below.)

[0024] (2) The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing of (1) characterized by further including REM: 0.000005 to 0.001%, the inclusions covered due to composition satisfying, by average concentration, furthermore (%T.REM)=0.3 to 1.0% and (%S)=0.05 to 0.2%,

[0025] where, (%T.REM) and (%S) respectively include the total of rare earth elements in the inclusions and the content of S (mass%). (Same below.)

[0026] (3) The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing of (1) or (2) characterized by further including B: 0.0005 to 0.002%.

[0027] (4) The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing of any one of (1) to (3) characterized by further including one or more of Cr: 0.05 to 1.0%, Ni: 0.05 to 1.0%, Cu: 0.05 to 1.0%, Ti: 0.001 to 0.25%, Nb: 0.001 to 0.25%, V: 0.001 to 0.25%, Mo: 0.05 to 1.0%, and Co: 0.1 to 2%.

Advantageous Effects of Invention

[0028] According to the present invention, it is possible to obtain high performance high carbon wire which can refine the inclusions after wire rolling, which can handle even tough applications such as saw wire, which is extremely low in wire breakage rate at the time of drawing, and which is excellent in fatigue characteristics after wire drawing as well.

Description of Embodiments

[0029] Below, the present invention will be explained in detail. First, details of the mechanism of the present invention will be explained. Note that, unless otherwise indicated, below, "%" will be deemed to mean "mass%".

[0030] The conventional technique for multi-component control of nonmetallic inclusions was a technique lowering the melting point and viscosity of silicate inclusions. In such silicate inclusions, Na and F are extremely strong in affinity. Seen from a micro viewpoint, Na ions and F ions are positioned close by and influence the melting point and viscosity of silicate inclusions as NaF molecules.

[0031] Oxides containing NaF start to melt at a temperature of 1200°C or less, while oxides to which only Na_2O is added and oxides to which only F (for example, CaF_2) is added do not start melting until a high temperature of over 1200°C. That is, by establishing the copresence of Na and F, an extremely low melting point can be realized.

[0032] This melting point of 1200°C or less is a temperature close to not only the blooming in the breakdown process of a continuously cast steel slab (1150 to 1300°C), but also to the wire rolling temperature (1000 to 1200°C). In the past, it was believed that the stretching of inclusions at the time of rolling occurred mainly in the blooming process. However, when Na and F are copresent in inclusions, the inclusions are stretched not only in the blooming process, but also in the wire rolling process. Therefore, by establishing the copresence of Na and F, it is possible to refine inclusions much more.

[0033] In nonmetallic inclusions, there is the potential for various crystal phases to be formed in accordance with the composition, but in actuality crystal phases are formed and become starting points of wire breakage etc. when growing large. As opposed to this, if adding NaF molecules, in addition to the effect of a drop in the melting point and a drop in the viscosity, there is the effect of a remarkable delay in the formation of crystal phases. As a result, the starting points of wire breakage are decreased, so the wire breakage rate at the time of drawing becomes extremely low.

[0034] Note that, the effect of Na and F on the stretchability of inclusions depends on the calculated amount of NaF in the inclusions. If the calculated amount of NaF increases, the stretchability is improved. Here, the "calculated amount of NaF" means the mass% of NaF in the inclusions when Na and F are bonded 1:1 in molar ratio.

[0035] When the balance of Na and F is poor and excessive Na or F is present, there is almost no effect on the stretchability of inclusions. For this reason, these are preferably added so that (%Na) and (%F) become, in terms of molar ratio, 1:1, that is, in terms of mass ratio, 1:0.83.

[0036] PLTs 8 to 11 disclose methods using oxides of alkali metals such as Na. However, none of these literature allude to the need to basically use silicate-based multi-component inclusions and establish copresence of Na and F. That is, the inventions of these literature and the present invention differ in technical idea.

[0037] Next, the reasons for setting the contents of the oxides forming the oxide-based inclusions in the present invention will be explained.

[0038] First, the reasons for limitation of the total oxygen amount in the steel will be explained. In wire with a total oxygen amount of over 30 ppm, the amount of nonmetallic inclusions becomes greater and wire breakage cannot be sufficiently avoided in worked materials used for tough applications, so the upper limit is made 30 ppm. On the other hand, if using a powerful deoxidizing material such as Al or Mg in a large amount, it is easy to make the total oxygen amount less than 16 ppm, but to control the composition of nonmetallic inclusions in the wire of the present invention, a total oxygen content of 16 ppm or more is necessary. If the total oxygen amount is less than 16 ppm or more than 30 ppm, the die life becomes extremely poor. The more preferable range of the total oxygen amount is 17 to 25 ppm.

[0039] Next, the compositions and types of the nonmetallic inclusions in the present invention will be explained.

[0040] The steel wire of the present invention is characterized in that inclusions satisfying ($\%SiO_2$)=40 to 95%, (%can) =0.5 to 30%, ($\%Al_2O_3$)=0.5 to 30%, (%MgO)=0.5 to 20%, and (%MnO)=0.5 to 10% and further satisfying (%Na)=0.2 to 7% and (%F)=0.17 to 8% (inclusions covered due to composition) in oxide-based nonmetallic inclusions of a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter (area converted to diameter) of 1 μm or more which are seen in the L direction cross-section of the wire (inclusions covered due to size) are 80% or more in terms of the number ratio (number of inclusions covered due to composition/number of inclusions covered due to size×100).

[0041] Inclusions with a short axis of less than 0.5 μm in the wire L cross-section are inclusions which are inherently small in size or which easily deform during rolling. Inclusions with a long axis of less than 1.0 μm and a circle equivalent diameter of less than 1.0 μm are inclusions which are inherently small in size. These inclusions tend to not become causes of deterioration of the drawability and fatigue characteristics.

[0042] Therefore, in the present invention, oxide-based nonmetallic inclusions with a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter of 1 μm or more, seen in the cross-section of a wire, were defined as inclusions for evaluation and are called "inclusions covered due to size".

[0043] Next, the reasons for limitation of the ranges of composition will be explained for the inclusions covered due to composition.

[0044] To soften and refine the nonmetallic inclusions aimed at in the present invention, first, a multi-component oxide composition has to be put together. The oxide composition is based on a five-component system of SiO_2-CaO-Al_2O_3-MgO-MnO. Na and F are simultaneously included whereby for the first time the effects of softening and refining the nonmetallic inclusions are exhibited.

[0045] SiO_2 is an important oxide forming the basis of the silicate inclusions. If ($\%SiO_2$) is less than 40%, the base multi-component inclusions themselves will not become silicate inclusions and the effects of the present invention cannot be exhibited. If ($\%SiO_2$) exceeds 95%, the result no longer becomes multi-component inclusions and large sized SiO_2 causes deterioration of quality.

[0046] (%CaO) has to be made 0.5% or more to obtain the effect of reduction of the melting point and viscosity by formation of multi-component inclusions. If (%CaO) exceeds 30%, CaO-rich hard inclusions are formed and a deterioration of quality occurs.

[0047] Al_2O_3 contributes to softening of inclusions if in a suitable quantity, but if exceeding 30% as ($\%Al_2O_3$), hard Al_2O_3 inclusions are formed and the quality greatly deteriorates. If ($\%Al_2O_3$) is less than 0.5%, the effect of the multi-component inclusions is not obtained.

[0048] (%MgO) has to be made 0.5% or more to obtain the effect of reduction of the melting point and viscosity by formation of multi-component inclusions. If (%MgO) exceeds 20%, olivine or foresterite ($2MgO \cdot SiO_2$) or other harmful inclusions are formed.

[0049] (%MnO) has to be made 0.5% or more to obtain the effect of reduction of the melting point and viscosity by formation of multi-component inclusions. If (%MnO) exceeds 10%, the inclusions become not silicate inclusions, but Spessartite (SiO_2-MnO-Al_2O_3) inclusions and the effects of addition of Na and F are no longer exhibited.

[0050] Na and F are extremely important ingredients in the present invention. If (%Na) is less than 0.2%, there is no effect of improvement of stretchability of inclusions. On the other hand, if (%Na) is over 7%, the problems arise that the effect becomes saturated and the amount of dust generated when adding Na rapidly rises. The content is preferably less than 4%.

[0051] Further, if (%F) is less than 0.17%, there is no effect of improvement of stretchability of inclusions. If (%F) is over 8%, the effect becomes saturated and problems such as a rapid increase in the refractory melt loss become greater. Note that, as explained above, Na and F exhibit their effects after forming NaF molecules in the inclusions, so they are preferably added so that the molar ratio of Na and F in the nonmetallic inclusions becomes 1:1, that is, by mass ratio, (%Na):(%F) become close to 1:0.83.

[0052] Note that, when counting the oxide-based nonmetallic inclusions (inclusions covered due to size) with a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter of 1 μm or more, seen in the cross-section of a wire, it is necessary that the number ratio of inclusions which satisfy the above composition among the inclusions covered due to size (inclusions covered due to composition) (number of inclusions covered due to composition/number of inclusions covered due to size×100) be 80% or more.

[0053] The number ratio falling under 80% means that the effect of stretching of inclusions by Na+F cannot be enjoyed. Further, falling under 80% means, for example, the presence of a certain amount of inclusions of compositions not belonging to multi-component inclusions such as MgO-based or Al_2O_3-based hard inclusions. As a result, the drawability and the fatigue characteristics after wire drawing are impaired.

[0054] The reason for defining the size of the inclusions is to count only inclusions of a size causing deterioration of the drawability and fatigue characteristics.

[0055] In the present invention, it is possible to add both Na and F into the steel, include both Na and F in the silicate-based multi-component oxide-based inclusions, and control the composition of inclusions so as to secure excellent drawability and fatigue characteristics after wire drawing. Recently, applications are increasing in which the steel wires are drawn more finely. In such applications, the high carbon steel wires of the present invention exhibit particularly excellent performance.

[0056] The method of addition of Na and F may be to add them as an NaF compound. It is also possible to add Na and F separately (for example, Na_2CO_3 and CaF_2 etc.)

[0057] Note that, when adding F, if simultaneously adding it with metal Si, SiF_4 is formed and gasifies and the yield of F deteriorates, so this should be avoided.

[0058] By controlling the (%T.REM) (total content of La, Ce, Nd, and other rare earths) and (%S) in the nonmetallic inclusions, the drawability can be further improved. The reason is as follows:

[0059] REM (La, Ce, Nd, etc.) is strong in affinity with S, fixes S in the form of REM oxysulfide (REM_2O_2S), and is taken into the multi-component inclusions. Due to this, it is possible to reduce the amount solid solution S in the steel and precipitation of MnS is suppressed. The MnS which is precipitated in the steel sometimes becomes the starting point of breakage during drawing. By suppressing this precipitation, the drawability and the fatigue characteristics after wire drawing are improved.

[0060] The (%T.REM) of the inclusions covered due to composition should be controlled to 0.3 to 1.0%, while (%S) should be controlled to 0.05 to 0.2% in range. If (%T.REM) is less than 0.3%, the S fixing ability is insufficient, while if over 1.0%, the concentration of REM oxides in the nonmetallic inclusions increases and the stretchability is sometimes not sufficiently improved. Further, if (%S) is less than 0.05%, the fixed amount of S is too small and there is no effect, while if over 0.2%, CaS etc. is formed in the nonmetallic inclusions and the stretchability is sometimes not sufficiently improved.

[0061] Note that, wire breakage starting from MnS is less frequent compared with wire breakage starting from oxide-based nonmetallic inclusions. Therefore, first, it is necessary to suitably control the composition of oxide-based nonmetallic inclusions in the steel.

[0062] Next, the provisions on the composition of ingredients of the steel of the present invention will be explained. So-called killed steel is used for wire which is used as high carbon steel wire such as_the piano wire of JISG3502, hard steel wire of JISG3506, and oil tempered wire for valve springs of JISG3561. Considering these JIS standards, ease of manufacture, and practical aspects, the ranges of ingredients are defined as follows in the present invention.

[0063] That is, the steel is steel which contains, by mass%, C: 0.5 to 1.2%, Si: 0.15 to 2.5%, Mn: 0.20 to 0.9%, $P \leq 0.025\%$, S: 0.004 to 0.025%, Al: 0.000005 to 0.002%, Ca: 0.00001 to 0.002%, Mg: 0.00001 to 0.001%, Na: 0.000005 to 0.001%, and F: 0.000003 to 0.001% and which contains, in accordance with need, one or more types of Cr: 0.05 to 1.0%, Ni: 0.05 to 1.0%, Cu: 0.05 to 1.0%, Ti: 0.001 to 0.25%, V: 0.001 to 0.25%, Nb: 0.001 to 0.25%, Mo: 0.05 to 1.0%, and Co: 0.1 to 2%.

[0064] Further, if including REM: 0.000005 to 0.001%, the effect of the present invention becomes larger. Furthermore, if adding B: 0.0005 to 0.002%, steel which is much more excellent in drawability and the fatigue characteristics after wire drawing is obtained.

[0065] C is an element which is economic and effective in strengthening the steel. To obtain the strength required as a hard steel wire, 0.5% or more is necessary. However, if over 1.2%, the steel falls in ductility and becomes brittle and secondary working becomes difficult, so the content is made 1.2% or less. The more preferable concentration of C is 0.51 to 1.1%.

[0066] Si and Mn are required for deoxidation and control of the composition of inclusions. If Si is less than 0.15% and Mn is less than 0.20%, there is no effect. Further, while also effective as a steel strengthening element, if Si is over 2.5% and Mn is over 0.9%, the steel becomes brittle. The more preferable ranges of Si and Mn are respectively 0.16 to 2.3% and 0.25 to 0.85%.

[0067] P causes degradation of the wire drawability in high carbon steel and further causes degradation of the ductility after wire drawing. Accordingly, the content of P has to be made 0.025% or less, more preferably is 0.020% or less.

[0068] S also causes degradation of the wire drawability and further causes degradation of the ductility after wire drawing. On the other hand, to secure descaling of the steel material, it is necessary to secure a certain extent of concentration of S or more. Accordingly, the content of S is 0.004 to 0.025%, preferably 0.005 to 0.020%.

[0069] Al is an element which influences the composition of inclusion of the present invention. If too great or too small, a predetermined composition of inclusions cannot be obtained. Accordingly, the concentration of Al is 0.000005 to 0.002%, preferably 0.0002 to 0.001%.

[0070] Ca is also an element which influences the composition of inclusions of the present invention. If too great or too small, a predetermined composition of inclusions cannot be obtained. Accordingly, the concentration of Ca is made 0.00001 to 0.002%, preferably 0.000013 to 0.0015%.

[0071] Mg also is an element which influences the composition of inclusions of the present invention, If too great or too small, a predetermined composition of inclusions cannot be obtained. Accordingly, the concentration of Mg is made 0.00001 to 0.001%, preferably 0.000011 to 00008%.

[0072] Further, Na and F are extremely important ingredients in the composition of inclusions of the present invention. The concentrations of Na and F in the steel influences the composition of inclusions.

[0073] Na is an element which influences the composition of inclusions of the present invention. If too great or too small, a predetermined composition of inclusions cannot be obtained. Accordingly, the concentration of Na is made 0.000005 to 0.001%, preferably 0.000007 to 0.0005%.

[0074] F is also an element which influences the composition of inclusions of the present invention. If too great or too small, a predetermined composition of inclusions cannot be obtained. Accordingly, the concentration of F is made 0.000003 to 0.001%, preferably 0.000005 to 0.0005%.

[0075] The steel of the present invention preferably further contains the following ingredients.

[0076] Cr has the effect of refining the pearlite and raising the strength of the steel. The amount required for obtaining this effect is 0.05%. Addition of this or more is preferable. However, if adding over 1.0%, the ductility is impaired, so the upper limit is made 1.0%.

[0077] Ni strengthens the steel by effects similar to Cr. To obtain these effects, addition of 0.05% or more is preferable. If adding over 1.0%, the ductility falls, so the upper limit is made 1.0% or less.

[0078] Cu has the effect of improve the scale characteristics and corrosive fatigue characteristics of the wire. To obtain this effect, addition of 0.05% or more is preferable. If adding over 1.0%, the ductility falls, so the upper limit is made 1.0% or less.

[0079] Ti, Nb, and V have the effect of raising the strength of wire by precipitation strengthening. In each case, there is no effect if less than 0.001%, while if over 0.25%, precipitation embrittlement is caused. Accordingly, the content is made 0.001 to 0.25%. Further, these elements are effective if added to reduce the γ grain size at the time of patenting.

[0080] Mo is an element which improves the hardenability of steel. In the case of the present invention, it is possible to raise the strength of the steel by adding this, but addition of an excessive amount causes the steel to excessively harden and makes working it difficult. Accordingly, the range of addition of Mo is made 0.05 to 1.0%.

[0081] Co, by inclusion in 0.1 to 2%, has the effect of suppressing the formation of pro-eutectoid cementite of the hyper-eutectoid steel whereby the ductility is improved.

[0082] B improves the hardenability of steel and, when present in the austenite in the solid solution state, concentrates at the grain boundaries to suppress the formation of ferrite, degenerate pearlite, bainite, and other nonpearlite precipitates and thereby improve the drawability. If the amount of addition is too small, this effect cannot be obtained, so the lower limit is made 0.0005%. On the other hand, if adding too much, the precipitation of coarse $Fe_3(CB)_6$ carbides in the austenite is promoted and the drawability is adversely influenced. Therefore, the upper limit is made 0.002%.

[0083] An REM is an element which influences the composition of inclusions of the present invention. If the REM is too great or too small, the predetermined composition of inclusions for improving the drawability cannot be obtained, so the content is made 0.000005 to 0.001%.

[0084] Next, the method of production of the high carbon steel wire of the present invention will be explained.

[0085] The steel of the present invention can be produced by tapping molten steel which has finished being refined in a converter or electric furnace into a ladle, then refining it by simplified ladle refining. As the simplified ladle refining, CAB (capped argon bubbling), SAB (shield argon bubbling), CAS (adjustment of ingredients by SAB) which are described in NPLT 1 may be used.

[0086] To make the total oxygen amount in the steel 30 ppm or less, it is effective to suppress as much as possible the contamination by converter slag which flows out from the converter to the ladle at the time of tapping and, further, to secure a sedation time of simplified ladle refining (time from end of ladle refining to start of continuous casting) of about 20 to 40 minutes, and to promote flotation and separation of oxides. Further, it is also effective to prevent oxidation by air of the molten steel between the ladle and the tundish and between the tundish and the continuous casting mold.

[0087] On the other hand, to make the total oxygen amount in the steel 16 ppm or more, it is possible to not add the strong deoxidizing element Al or Mg into the steel as much as possible, to keep the addition of Ti to the minimum necessary extent as well, and to not perform treatment of simplified ladle refining for a long period of time.

[0088] Specifically, the melting of the synthetic slag and agitation of the molten steel, the secondary deoxidation and fine adjustment of ingredients and adjustment of molten steel temperature, and argon bubbling in the ladle are assumed to take 25 to 40 minutes. Further, argon bubbling in the ladle is used to uniformly mix the ingredients and cooling materials and promote the flotation and separation of inclusions.

[0089] If performing vacuum degassing and other full-scale ladle refining, the possibility of the total amount of oxygen in the steel becoming less than 16 ppm becomes higher, so this is not preferable.

[0090] Making the inclusions covered due to size in the steel with an ($\%Al_2O_3$) of 30% or less ones of a number ratio of 80% or more requires effort to prevent contamination of the steel by Al. It is preferable to not use Al as a deoxidizing material of course and to use an ferroalloy with a low Al content for the Fe-Si and Si-Mn of the ferroalloy which is added at the time of tapping.

[0091] For example, usual Fe-Si contains about 1.5% of Al, but low Al-Fe-Si with an Al content of about 0.01 to 0.10% can be preferably used. Further, even if using refractories with a small alumina content as ladle refractories, it is effective to introduce inclusions with an (%Al_2O_3) of 30% or less in a number ratio of 80% or more.

[0092] Note that, there is always some contamination by Al derived from the Al in the ferroalloy which is added to the steel or the alumina in the ladle or tundish refractories, so it is possible to make the inclusions with an (%Al_2O_3) of 0.5% or more a number ratio of 80% or more.

[0093] The (%CaO) and (%SiO_2) in the inclusions can be made ones in the ranges of the present invention by adjusting the contents of CaO and SiO_2 in the slag on the ladle in simplified ladle refining and by employing production conditions for making the total amount of oxygen in the above steel 30 ppm or less.

[0094] Specifically, it is possible to adjust the ingredients and amounts of the SiO_2-CaO-based synthetic slag which is added to the ladle so as to adjust the basicity of the ladle slag (CaO/SiO_2 mass ratio). The basicity of the ladle slag is preferably 0.9 to 1.3. Further, by adopting production conditions giving a total oxygen amount in the steel of 30 ppm or less, it is possible to prevent an increase in the (%SiO_2) of inclusions due to oxidation of the Si ingredient in the steel.

[0095] Note that, regarding the point of making the inclusions ones with (%MgO) of 0.5 to 20% and (%MnO) of 0.5 to 10%, it is possible to make the inclusions ones in the range of the present invention by smelting of ordinary steel based on contamination from the sources of MgO in the refractories and oxidation of Mn in the steel.

[0096] Regarding the point of making the inclusions ones with (%Na)=0.2 to 7% and (%F)=0.17 to 8%, as explained above, by adding Na and F into the steel, it is possible to include both Na and F in the inclusions within the ranges of the present invention.

[0097] At this time, the method of addition of Na and F may be to add them as an NaF compound or to add Na and F separately (for example, Na_2CO_3, CaF_2, etc.) Note that, when adding F, if simultaneously adding it with metal Si, SiF_4 is formed and gasifies and the yield of F deteriorates, so this should be avoided.

[0098] To make the (%T.REM) in the inclusions 0.3 to 1.0% and make the (%S) 0.05 to 0.2%, it is sufficient to add REM into the steel in an amount corresponding to several ppm. The REM which is added to the steel reacts with the S in the steel to form REM oxysulfides and join with the silicate-based inclusions. As a result, in the inclusions covered due to composition, it is possible to include (%T.REM)=0.3 to 1.0%, (%S)=0.05 to 0.2% in average concentration.

Examples

[0099] The smelting of the present examples was performed by an LD converter. When tapping steel from an LD converter to a ladle, a so-called "dart" type converter slag sealing tool is used to keep the outflow of LD slag at a small amount (50 mm thickness or less).

[0100] Further, at the time of tapping, a carburization material for adjusting the ingredients of C, Si, and Mn and Fe-Si, Fe-Mn, Si-Mn, or other deoxidizing ferroalloy were added. For the deoxidizing ferroalloy, one containing as little Al, Mg, or other powerful deoxidizing element as possible was used. Further, during the tapping or after the tapping, argon gas was blown in from the ladle bottom.

[0101] The molten steel in the ladle after receiving the steel was deoxidized by the Si, Mn, etc., that is, was so-called "killed steel". This ladle was moved to the position for molten steel refining, then SiO_2-CaO-based synthetic slag was added to the ladle, then argon was blown from the ladle bottom to agitate the molten steel in the ladle and perform CAB simplified ladle refining.

[0102] Next, the secondary deoxidizing material was added to the molten steel as ferroalloy. The secondary deoxidizing material included metal Ca, Al, Mg, Si, etc. In accordance with need, Na, F, and REM were added to the steel in the ladle. When adding both Na and F, NaF was added, when adding Na alone, Na_2CO_3 was added, and when adding F alone, CaF_2 was added. When adding F, it is added at a timing separate from the addition of the alloy containing Si or secondary deoxidizing material.

[0103] After adding the secondary deoxidizing material, the ingredients were further finally adjusted and the refining of molten steel in the ladle was ended. After finishing refining the ladle molten steel, a suitable sedation time (20 to 40 minutes or so) so that the total oxygen amount in the steel becomes 16 to 30 ppm was secured, then continuous casting was performed. The molten steel was continuously cast from the ladle through a tundish, but at that time, to suppress as much as possible the oxidation by air between the ladle and tundish and inside the tundish, inert gas was used to seal the system. The obtained steel bloom was passed through a bloom heating furnace, then bloomed, the steel bloom was rolled to billet, and the steel billet was straightened, then it was passed through a heating furnace and rolled to produce 5.5 mmϕ wire.

[0104] The number and composition of nonmetallic inclusions were investigated by cutting out samples of 0.5 meter length from one coil of 5.5 mmϕ wire, cutting out small samples of 11 mm length from any 10 locations in the L direction (length direction), and investigating the entire surfaces at the longitudinal cross-sections passing through the center axes in the length direction. The number and composition of nonmetallic inclusions were determined by obtaining oxide-based nonmetallic inclusions of a short axis of 0.5 μm or more, a long axis of 1.0 μm or more, and a circle equivalent diameter of 1 μm or more as "inclusions covered due to size" and analyzing the compositions of the individual inclusions by X-ray spectroscopy.

[0105] Among the inclusions covered due to size, the inclusions in the range of composition of the present invention are referred to as the "inclusions covered due to composition". These were evaluated for the number ratio (number of inclusions covered due to composition/number of inclusions covered due to size×100). Further, the average composition of all of the inclusions covered due to size was also calculated. However, for REM and S, the average composition of the inclusions covered due to composition was calculated.

[0106] After that, 5.5 mmϕ wires were drawn to 0.175 mmϕ or less and investigated for drawing characteristics and die life. The drawing characteristics were evaluated by the frequency of breakage for a certain amount of drawing as the "wire breakage index". A wire breakage index of 5 or less was considered good. The die life was evaluated indexed to the minimum lifetime allowable for materials in current processes as 100. The longer the lifetime, the greater the index. A die life index of 100 or more was good.

[0107] Furthermore, to evaluate the fatigue characteristics, wires drawn to 0.175 mmϕ were subjected to rotating fatigue tests. In the rotating fatigue tests, the stress was changed in various ways and the number of repetitions until breakage was investigated. The stress at which wire breakage occurs with 100000 repetitions was corrected by the coefficient of tension of a mechanical test and evaluated as the stress index. A stress index of 15 or more was judged as good.

[0108] Tables 1 to 4 show the results of invention examples and comparative examples. Numerical values which are outside the ranges of the present invention are underlined.

Table 1

		Chemical ingredients (wt%)																			ppm
	No	C	Si	Mn	P	S	Al	Ca	Mg	Na	F	REM	Cr	Ni	Cu	Ti	V	Nb	Mo	Co	B	Total oxygen am't
Inv. ex.	1	0.72	0.18	0.51	0.018	0.022	0.000450	0.000250	0.000150	0.000006	0.000005	0.000001	-	-	-	-	-	-	-	-	-	24
	2	0.82	0.18	0.51	0.010	0.021	0.000400	0.000300	0.000420	0.000250	0.000200	0.000002	-	-	-	-	-	-	-	-	-	22
	3	0.92	0.20	0.30	0.012	0.019	0.000300	0.001000	0.000230	0.000300	0.000300	0.000000	0.50	-	-	-	-	-	-	-	-	23
	4	0.96	0.20	0.30	0.011	0.015	0.000400	0.000410	0.000180	0.000100	0.000080	0.000001	0.20	-	-	-	-	-	-	-	-	21
	5	0.81	2.10	0.31	0.015	0.021	0.000010	0.000030	0.000040	0.000010	0.000080	0.000000	0.24	-	-	-	-	-	-	-	-	15
	6	0.52	0.25	0.31	0.021	0.015	0.000330	0.000560	0.000200	0.000800	0.000800	0.000001	-	-	-	-	-	-	-	-	-	28
	7	0.72	1.75	0.33	0.024	0.018	0.000006	0.000020	0.000020	0.000440	0.000500	0.000000	-	-	-	-	-	-	-	-	-	17
	8	1.18	0.20	0.70	0.012	0.025	0.000350	0.000230	0.000090	0.000180	0.000150	0.000080	-	-	-	-	-	-	-	-	-	16
	9	0.75	1.50	0.75	0.013	0.023	0.000060	0.000100	0.000100	0.000130	0.000120	0.000210	-	-	-	-	-	-	-	-	-	26
	10	0.82	0.25	0.88	0.018	0.019	0.000900	0.000160	0.000120	0.000190	0.000160	0.000140	-	-	-	-	-	-	-	-	-	22
	11	0.62	1.90	0.49	0.022	0.024	0.000020	0.000050	0.000030	0.000270	0.000200	0.000008	-	-	-	-	-	-	-	-	-	15
	12	0.77	0.18	0.53	0.010	0.018	0.000350	0.000180	0.000900	0.000090	0.000080	0.000060	-	-	-	-	-	-	-	-	-	29
	13	0.82	0.18	0.53	0.015	0.022	0.000400	0.000190	0.000150	0.000330	0.000300	0.000070	-	-	-	-	-	-	-	0.50	-	22
	14	0.73	0.22	0.70	0.016	0.021	0.000180	0.000700	0.000550	0.000009	0.000006	0.000900	0.18	-	0.24	-	-	-	-	-	-	28
	15	0.83	0.19	0.50	0.022	0.018	0.000300	0.000760	0.000170	0.000060	0.000030	0.000600	0.24	-	-	0.009	0.008	-	-	-	-	28
	16	0.71	0.30	0.49	0.010	0.025	0.000400	0.000200	0.000070	0.000090	0.000090	0.000220	-	-	-	-	0.003	0.007	-	-	-	25
	17	0.81	0.22	0.51	0.009	0.023	0.000270	0.000280	0.000330	0.000510	0.000440	0.000160	-	0.92	0.22	-	-	-	-	-	-	29
	18	0.95	0.15	0.50	0.016	0.018	0.000250	0.000220	0.000630	0.000140	0.000150	0.000090	-	-	-	-	-	0.009	0.08	-	-	21
	19	0.72	0.20	0.50	0.015	0.018	0.000380	0.000800	0.000050	0.000210	0.000160	0.000290	-	-	-	-	-	-	-	-	0.0007	20
	20	0.82	0.19	0.49	0.012	0.020	0.000400	0.000340	0.000510	0.000170	0.000140	0.000170	-	-	-	-	-	-	-	-	0.0015	21
	21	0.71	0.18	0.50	0.011	0.021	0.000200	0.001200	0.000600	0.000050	0.000040	0.000100	0.25	-	-	-	-	-	-	-	0.0009	25
	22	0.72	0.20	0.50	0.010	0.018	0.000390	0.000200	0.000060	0.000310	0.000260	0.000450	0.20	-	0.20	-	-	-	-	-	0.0018	19
	23	0.72	0.21	0.51	0.013	0.019	0.000340	0.000800	0.000080	0.000220	0.000220	0.000350	0.20	-	-	-	-	0.010	0.01	-	0.0010	20
	24	0.71	0.20	0.50	0.015	0.015	0.000260	0.000440	0.000660	0.000140	0.000100	0.000120	0.25	-	-	0.010	0.008	-	-	-	0.0008	24

Table 2 (Continuation of Table 1)

	No	Ratio of inclusions (%)*1	Wire breakage rate index	Die life index	Rotating fatigue stress index	Composition of nonmetallic inclusions (wt%)*2								
						SiO_2	MnO	Al_2O_3	MgO	CaO	Na	F	T.REM	S
Inv. ex.	1	99	0	150	16	44.1	9.3	16.5	5.9	23.2	0.5	0.4	0.0	0.0
	2	96	0	140	15	43.8	5.9	13.6	8.6	22.9	2.5	2.2	0.0	0.0
	3	95	0	150	15	45.0	6.5	11.0	4.0	27.1	3.3	2.4	0.0	0.1
	4	99	0	130	16	49.1	8.2	14.1	3.1	22.8	1.2	1.0	0.0	0.1
	5	81	0	120	15	93.2	0.6	1.0	1.1	2.3	0.8	0.5	0.0	0.1
	6	94	0	160	17	49.8	2.3	11.1	3.9	20.2	6.5	4.4	0.0	0.0
	7	88	0	130	15	80.6	9.5	0.8	0.7	0.5	4.1	2.9	0.0	0.0
	8	96	0	200	16	51.0	5.3	11.7	4.2	23.9	1.6	1.6	0.4	0.1
	9	91	0	170	17	71.5	2.8	5.8	4.3	11.0	1.8	1.2	0.6	0.1
	10	99	0	170	18	43.7	3.7	24.7	5.5	16.4	2.7	2.0	0.5	0.2
	11	87	0	180	16	86.5	0.6	1.9	1.8	3.8	2.5	2.2	0.3	0.2
	12	96	0	210	18	45.6	3.8	12.4	17.1	17.5	1.4	1.4	0.5	0.1
	13	95	0	190	17	49.0	3.7	14.2	3.1	22.1	3.8	3.3	0.4	0.1
	14	96	0	180	16	44.8	6.4	8.3	9.2	28.1	0.9	0.9	0.9	0.2
	15	96	0	180	16	44.9	4.5	10.0	4.3	23.8	3.9	7.5	0.7	0.1
	16	99	0	230	18	50.3	7.1	14.5	2.4	20.0	2.6	2.2	0.5	0.2
	17	98	0	190	17	46.0	5.1	9.0	5.5	24.5	4.9	4.0	0.5	0.1
	18	94	0	210	19	57.0	3.4	8.5	7.9	15.0	3.9	2.7	0.5	0.1
	19	95	0	270	20	45.7	6.3	12.1	4.5	25.2	3.0	2.5	0.4	0.1
	20	96	0	290	19	43.7	4.0	13.4	8.4	24.1	2.8	2.7	0.5	0.2
	21	98	0	260	21	46.7	4.5	9.7	10.0	26.3	1.0	0.9	0.5	0.1
	22	99	0	270	20	53.1	3.2	13.3	3.5	21.0	2.5	2.4	0.6	0.1
	23	95	0	240	20	49.7	4.0	12.1	4.5	25.3	1.5	1.6	0.9	0.1
	24	94	0	280	21	47.3	6.6	10.8	7.4	23.1	1.8	2.0	0.5	0.1

*1: Ratio of nonmetallic inclusions which satisfy composition set forth in claim 1. *2: Average composition of all nonmetallic inclusions in observed field

Table 3

		Chemical ingredients (wt%)																			ppm
	No	C	Si	Mn	P	S	Al	Ca	Mg	Na	F	REM	Cr	Ni	Cu	Ti	V	Nb	Mo	Co	B	Total oxygen amount
Comp.ex.	25	0.81	0.25	0.55	0.010	0.015	0.000410	0.000300	0.000100	0.000001	0.000001	0.000001	-	-	-	-	-	-	-	-	-	16
	26	0.72	0.20	0.50	0.025	0.023	0.001500	0.000140	0.000120	0.000190	0.000002	0.000000	-	-	-	-	-	-	-	-	-	25
	27	0.82	0.22	0.50	0.013	0.021	0.000400	0.000900	0.000090	0.000003	0.000500	0.000000	-	-	-	-	-	-	-	-	-	18
	28	0.62	0.19	0.30	0.012	0.016	0.000180	0.000120	0.000450	0.000360	0.000330	0.000001	-	-	-	-	-	-	-	-	-	38
	29	0.75	0.21	0.80	0.009	0.018	0.001900	0.000180	0.000950	0.000230	0.002000	0.000270	-	-	-	-	-	-	-	-	-	19
	30	0.82	0.19	0.90	0.011	0.023	0.000510	0.000700	0.000550	0.000190	0.000160	0.000000	-	-	-	-	-	-	-	-	-	29
	31	0.73	1.52	0.49	0.022	0.024	0.000010	0.000040	0.000100	0.000500	0.000400	0.000001	-	-	-	-	-	-	-	-	-	28
	32	0.75	0.19	0.48	0.009	0.024	0.003000	0.000200	0.000070	0.000170	0.000130	0.000220	-	-	-	-	-	-	-	-	-	25
	33	0.70	0.20	0.49	0.014	0.030	0.000330	0.000280	0.000330	0.000510	0.000400	0.000700	-	-	-	-	-	-	-	-	-	21
	34	0.80	0.19	0.50	0.020	0.020	0.000430	0.000290	0.000410	0.000250	0.000200	0.001200	-	-	-	-	-	-	-	-	-	22

Table 4 (Continuation of Table 3)

	No.	Ratio of inclusions (%)*1	Wire breakage rate index	Die life index	Rotating fatigue stress index	Nonmetallic inclusions composition (wt%)*2								
						SiO_2	MnO	Al_2O_3	MgO	CaO	Na	F	T.REM	S
Comp. ex.	25	0	8	80	13	45.5	6.1	12.8	7.4	28.0	0.0	0.0	0.0	0.0
	26	0	6	90	13	46.0	2.2	15.2	10.1	23.1	3.0	0.0	0.0	0.0
	27	0	7	90	14	44.8	4.6	12.7	7.0	27.9	0.1	2.5	0.0	0.0
	28	98	4	30	8	52.1	9.9	7.8	5.8	19.7	2.4	2.0	0.0	0.0
	29	70	20	20	7	48.5	1.6	10.5	18.2	13.9	3.6	2.7	0.4	0.1
	30	40	8	80	12	37.2	8.5	13.3	11.6	24.6	2.2	2.2	0.0	0.0
	31	4	33	20	6	96.7	0.5	0.6	0.6	0.7	0.3	0.2	0.0	0.0
	32	77	60	10	5	42.7	3.1	32.4	1.1	16.9	1.7	1.5	0.3	0.2
	33	92	10	60	10	44.9	4.4	11.3	6.3	25.7	3.1	2.9	0.7	0.5
	34	94	18	20	7	46.1	4.2	11.7	4.9	25.4	2.9	3.0	1.5	0.2

[0109] In the Invention Example Nos. 1 to 24, good results could be obtained in each case. Nos. 8 to 18 are examples of addition of REMs in addition to Na and F. In this case, the die life and fatigue characteristics are improved. Furthermore, Nos. 19 to 24 are examples of addition of B to the steel. A further improvement in the die life and fatigue characteristics was confirmed.

[0110] Next, the results of the comparative examples will be explained. No. 25 is a case of no addition of Na and F, No. 26 is a case of addition of Na alone, and No. 27 is a case of addition of F alone. In each case, the number ratio of inclusions (number of inclusions covered due to composition/number of inclusions covered due to size×100, below referred to as the "number ratio of inclusions") was zero. The wire breakage index, die life, and fatigue characteristics all deteriorated compared with the invention examples.

[0111] No. 28 is the case where the seal in the tundish is insufficient, so the total oxygen amount becomes higher than the range of the present invention. The number of inclusions was large and the die life and fatigue characteristics deteriorated.

[0112] Nos. 29 to 32 are examples where the number ratio of inclusions fell below 80%. No. 29 is an example which uses refractories high in Al_2O_3 and MgO content, so a large number of Al_2O_3-based and MgO-based inclusions believed to be due to the refractories are present in the inclusions. As a result, the number ratio of inclusions fell and the wire breakage index, die life, and fatigue characteristics all deteriorated.

[0113] No. 30 is an example where the change in composition of the SiO_2-CaO-based synthetic slag caused the (%SiO_2) in the nonmetallic inclusions to drop, so the number ratio of inclusions fell, some hard inclusions appeared in the inclusions, and the wire breakage index, die life, and fatigue characteristics all deteriorated somewhat.

[0114] No. 31 is an example where the amount of outflow of LD slag was somewhat large, coarse inclusions of SiO_2 alone appeared in the deoxidizing process, and the (%SiO_2) in the nonmetallic inclusions increased. As a result, the number ratio of inclusions fell and the wire breakage index and fatigue characteristics deteriorated.

[0115] No. 32 is an example which used as a deoxidizing alloy not a low Al ferroalloy, but a high Al concentration usual ferroalloy. The (%Al_2O_3) in the nonmetallic inclusions increased. As a result, the number ratio of inclusions fell, a large number of hard Al_2O_3-based inclusions were formed, and the wire breakage index, die life, and fatigue characteristics were all extremely poor.

[0116] No. 33 is an example where the concentration of S in the steel is high, the (%S) in the nonmetallic inclusions is a higher value than the range of the present invention, and the wire breakage index, die life, and fatigue characteristics deteriorate.

[0117] No. 34 is an example where has too much REM added, so the (%T.REM) in the nonmetallic inclusions becomes a value higher than the range of the present invention and the wire breakage index, die life, and fatigue characteristics deteriorate.

Claims

1. High carbon steel wire rod excellent in drawability and the fatigue characteristics after wire drawing which contains, by mass%,
   C : 0.5 to 1.2%,
   Si: 0.15 to 2.5%,
   Mn: 0.20 to 0.9%,
   P ≤0.025%,
   S: 0.004 to 0.025%,
   Al: 0.000005 to 0.002%,
   Ca: 0.00001 to 0.002%,
   Mg: 0.00001 to 0.001%,
   Na: 0.000005 to 0.001%, and
   F: 0.000003 to 0.001%,
   has a total oxygen amount of 16 to 30 ppm, and which has a balance of Fe and unavoidable impurities,
   the high carbon steel wire **characterized in that** the number ratio of inclusions satisfying (%SiO_2)=40 to 95%, (%CaO)=0.5 to 30%, (%Al_2O_3)=0.5 to 30%, (%MgO)=0.5 to 20%, and (%MnO)=0.5 to 10% and further satisfying (%Na)=0.2 to 7% and (%F)=0.17 to 8% (below, referred to as "inclusions covered due to composition") in the oxide-based nonmetallic inclusions of a short axis of 0.5 μm or more,
   a long axis of 1.0 μm or more, and a circle equivalent diameter (area converted to diameter) of 1 μm or more which are seen in the L direction cross-section of the wire (below, referred to as "inclusions covered due to size"), that is, the number of inclusions covered due to composition/number of inclusions covered due to size×100, is 80% or more:

   where (%SiO_2), (%CaO), (%Al_2O_3), (%MgO), (%MnO), (%Na), and (%F) respectively are the contents of SiO_2, CaO, Al_2O_3, MgO, MnO, Na, and F in the inclusions (mass%).

2. The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing as set forth in claim 1 **characterized by** further including REM: 0.000005 to 0.001%, said inclusions covered due to composition satisfying, by average concentration, furthermore (%T.REM)=0.3 to 1.0% and (%S)=0.05 to 0.2%,
where, (%T.REM) and (%S) respectively include the total of rare earth elements in the inclusions and the content of S (mass%).

3. The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing as set forth in claim 1 or 2 **characterized by** further including B: 0.0005 to 0.002%.

4. The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing as set forth in claim 1 or 2 **characterized by** further including one or more of:

Cr: 0.05 to 1.0%,
Ni: 0.05 to 1.0%,
Cu: 0.05 to 1.0%,
Ti: 0.001 to 0.25%,
Nb: 0.001 to 0.25%,
V: 0.001 to 0.25%,
Mo: 0.05 to 1.0%, and
Co: 0.1 to 2%.

5. The high carbon steel wire excellent in drawability and the fatigue characteristics after wire drawing as set forth in claim 3 **characterized by** further containing one or more of
Cr: 0.05 to 1.0%,
Ni: 0.05 to 1.0%,
Cu: 0.05 to 1.0%,
Ti: 0.001 to 0.25%,
Nb: 0.001 to 0.25%,
V: 0.001 to 0.25%,
Mo: 0.05 to 1.0%, and
Co: 0.1 to 2%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/054971

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21C7/04*(2006.01)i, *C21C7/06*(2006.01)i, *C22C38/06*(2006.01)i, *C22C38/54*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C1/00-49/14, C21C7/04, C21C7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-197812 A (Honda Motor Co., Ltd.), 09 August 2007 (09.08.2007), & US 2007/0144619 A1 & EP 1803831 A2 & CN 101008069 A	1-5
A	JP 2007-289965 A (Kobe Steel, Ltd.), 08 November 2007 (08.11.2007), (Family: none)	1-5
A	JP 62-33094 A (Daido Steel Co., Ltd.), 13 February 1987 (13.02.1987), (Family: none)	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 22 May, 2012 (22.05.12)	Date of mailing of the international search report 29 May, 2012 (29.05.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 5722969B PCT **[0014]**
- JP 55024961 A **[0014]**
- JP 54007252 B **[0014]**
- JP 50081907 A **[0014]**
- JP 57035243 B **[0014]**
- JP 4008499 B **[0014]**
- JP 3294245 A **[0014]**
- JP 2654099 A **[0014]**
- JP 3719131 A **[0014]**
- JP 2005029888 A **[0014]**
- JP 4315825 B **[0014]**

Non-patent literature cited in the description

- Iron-making and Steel-making. Iron and Steel Institute of Japan ed. Third Edition Iron and Steel Handbook. 690 **[0015]**